X-Ray Absorption Spectroscopy Studies of Actinide Speciation in Nuclear Materials

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Overview

The speciation of actinides in various materials related to the disposition of nuclear waste was investigated using synchrotron-based x-ray absorption techniques. Materials examined include a U^{235}-bearing metal fragment recovered from a DOD site, Th- and U-templated ion exchange resins developed for nuclear materials separations, and U-metabolizing bacteria.

X-Ray Absorption Spectroscopy

- Utilizes x-rays from synchrotron source to probe local structure. High intensity, broad spectral range. Spectra can be separated into regions containing different information – XANES and EXAFS
- XANES - X-Ray Absorption Near Edge Structure, region between absorption edge and start of EXAFS oscillations, up to 40 eV above edge. Absolute position of edge contains information on oxidation state, vacant orbitals, electronic configuration, and site symmetry
- EXAFS - X-ray Absorption Fine Structure, region above absorption edge. Backscattering of photoelectrons are created by absorption of x-ray effect absorption, creating oscillations used to determine atomic number, distance, and coordination number of nearest neighbors

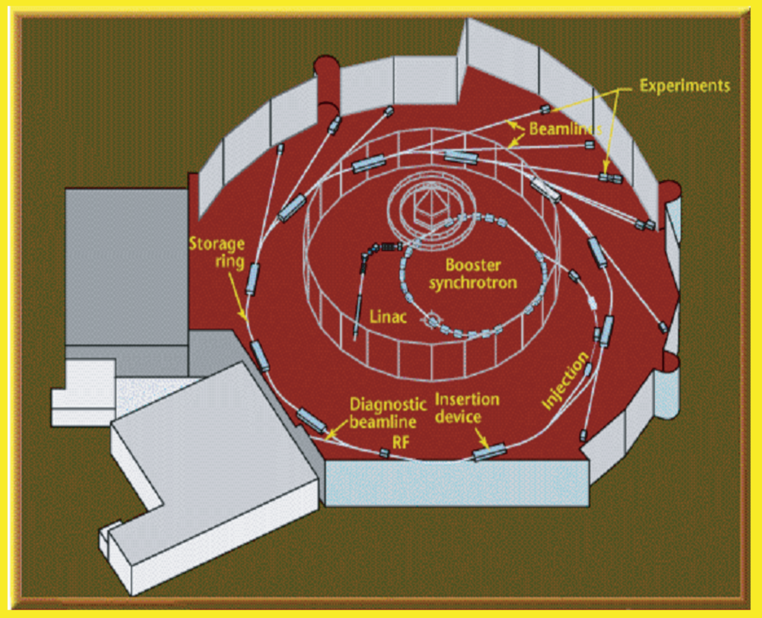


Figure 1. Schematic of the Advanced Photon Source (APS), a synchrotron at ANL

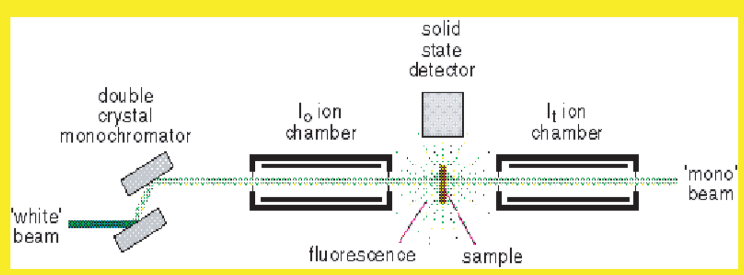


Figure 2. Detection method. Incoming x-ray energy is tuned using a monochromator. Intensity is monitored before and after sample interaction.

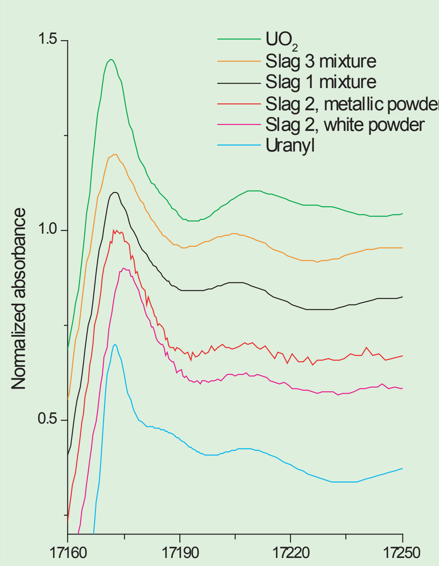
Nuclear Materials in the Environment: "USAF HEU"

Three samples recovered from a USAF site after 40 years in the ground. The samples contain up to 2 wt% U^{235} in a metallic matrix.

Sample	wt% U^{235}	Sampling location
1	2.1	Surface
2	0.1	Interior (metallic powder)*
		Interior (white powder)*
3	0.9	Surface

*Interior piece pulverized in a grinder and separated into two components

USAF HEU slag sample.



Uranium L_3 edge XANES

Methodology

Pulverized samples from various locations on the slags were scanned on the Uranium L_3 edge to k=14.

Results

XANES spectra reveal the uranium is a combination of uranyl and a less oxidized species. Analysis of the EXAFS spectra confirms this. More knowledge of the elemental composition of the materials is needed for final analysis.

Future Work

Samples will be dissolved and analyzed for elemental content. In addition, U^{235} content will be mapped.

Actinide Templated Resins

To create greater selectivity for the target ion in separation processes, molecularly imprinted resins were synthesized by way of a polymerization technique. Uranyl and thorium templated resins have shown fast kinetics and good separation efficiencies in previous studies. Lanthanides have also been used as homologs for americium and curium. The structures of uranyl, thorium, and samarium imprinted resins were investigated in this study. Nontemplated samples were synthesized with no metal presentand did not undergo the polymerization process.

50 mg samples of loaded resins were ground and mixed in a 200 mg inert matrix and placed in an Al window. The samples were analyzed at the L_3 edges.

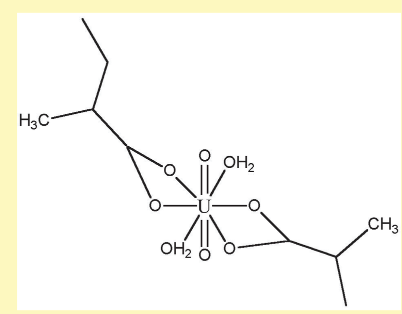
Uranyl Templated Resins

Samples:

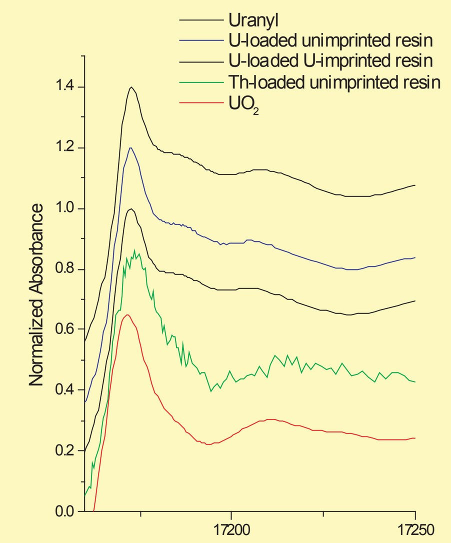
Uranium templated
Nontemplated, uranium sorbed
Nontemplated, thorium sorbed

Results

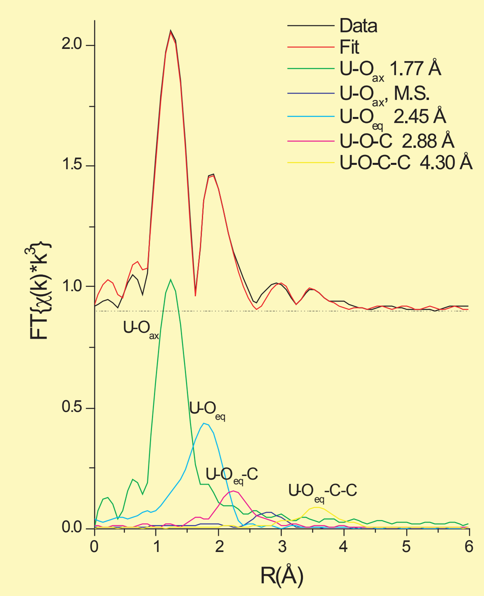
The uranium loaded resins are uranyl, as expected. XANES spectra showed the uranium contamination found in the thorium resin is U(IV), indicating that the contamination was in the thorium stock. EXAFS analysis of this sample was also consistent with UO_2. The resin structure is consistent with the proposed structure shown below.



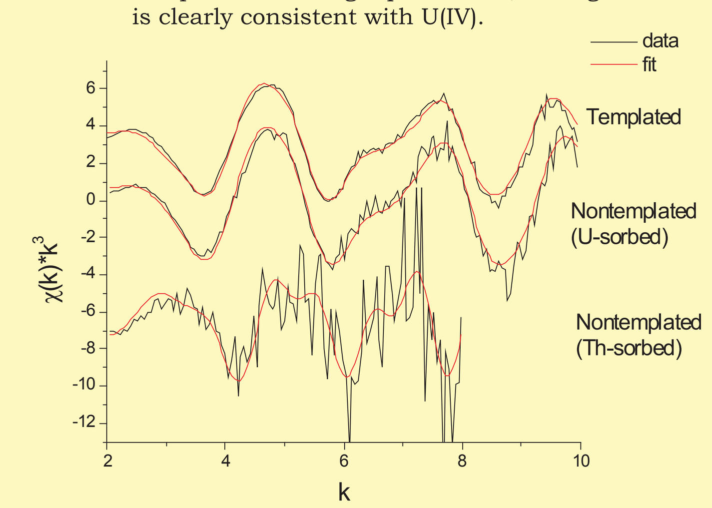
Expected Uranyl templated resin structure.This is a small segment of thepolymer chain.



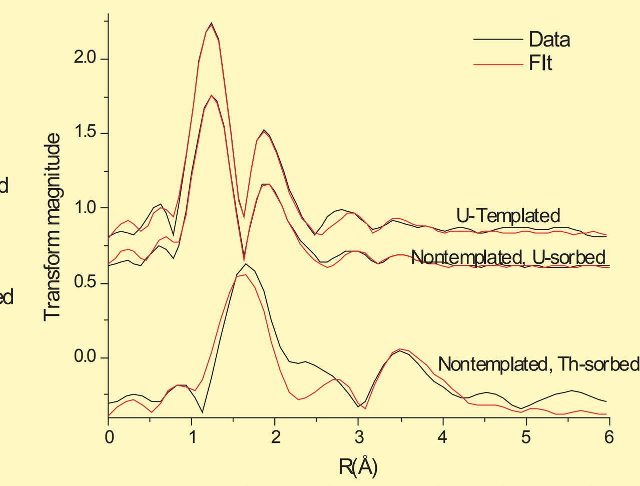
Uranium L_3 XANES. Note the Th-loaded sample. This is from contamination in the sample. Even though quite dilute, the signal is clearly consistent with U(IV).



Deconvolution of the Uranium-templated nonreleased sample fit.



EXAFS data and fits. Once again, the Th-loaded sample is quite different. The phase shift of the first peak is also indicative of U(IV).

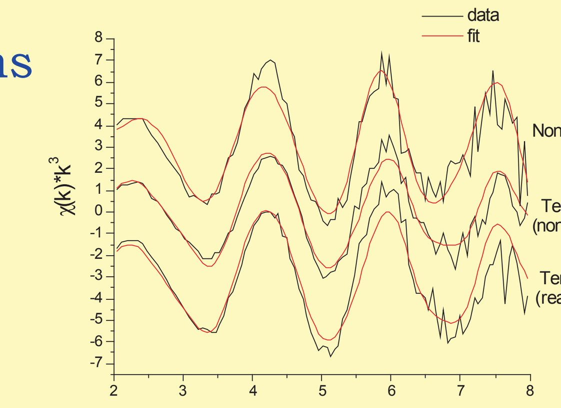


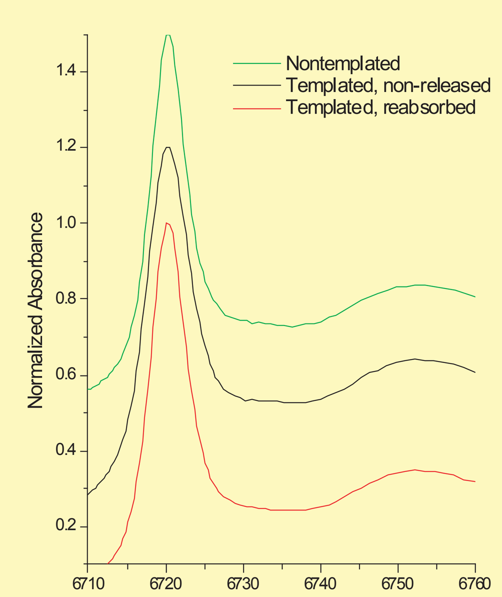
Fourier transforms of EXAFS data.The U-O bond length for UO_2 is significantly longer than the U=O axial bonds in uranyl.

Samarium Templated Resins

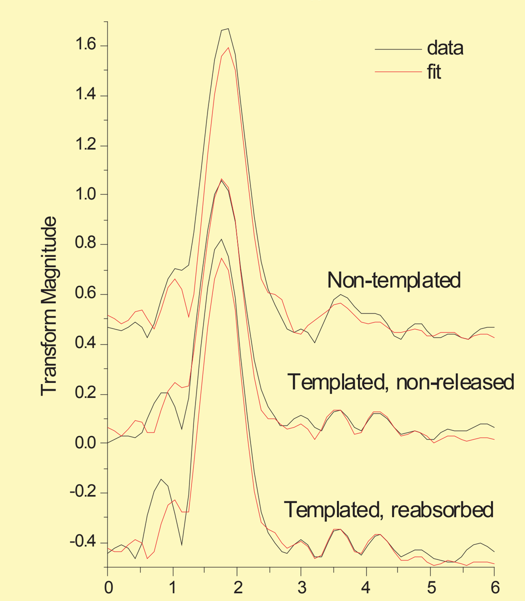
Samples:

Samarium templated, nonreleased
Samarium templated, reabsorbed
Nontemplated, thorium sorbed





Samarium L_3 XANES. All three samples are Sm(III).



Samarium EXAFS (top) and Fourier transforms of data and the corresponding fits.

Results

The Sm samples were scanned to k=9, limiting analysis to the first shell. However, differences in the structures of the templated and nontemplated resins can still be seen. XANES spectra show no change in oxidation state between the samples. EXAFS oscillations of the nontemplated sample are slightly shorter wavelength, indicating lengthening of the Sm-O bond.

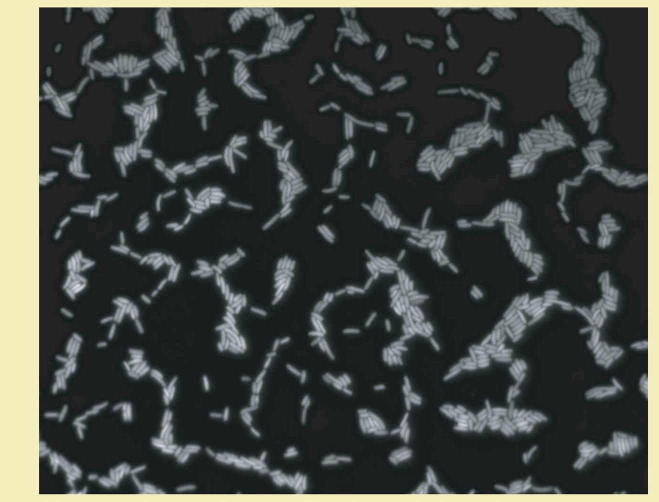
Sample	R(Sm-O), Å
Nontemplated	2.48
Templated (nonreleased)	2.43
Templated (reabsorbed)	2.43

Uranium uptake by *S. Putrefaciens*

The bacteria *Shewanella putrefaciens*, a widely distributed species known to utilize several elements such as iron, manganese and sulfur as electron acceptors. In an anoxic environment, *S. putrefaciens* can also use uranium, reducing its oxidation state from hexavalent to tetravalent, by the following reaction:

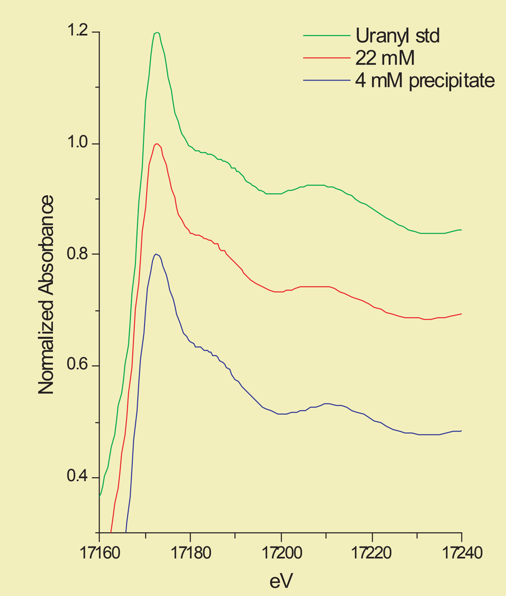
$$H_2 + U(VI) \rightarrow 2H^+ + U(IV)$$

Tetravalent uranium (UO_2) is insoluble, and the reduction reaction is a favorable one. Uranium in this state will tend to remain immobile in soil, while the more soluble hexavalent uranium will dissolve, leading to an increase in area of contamination.

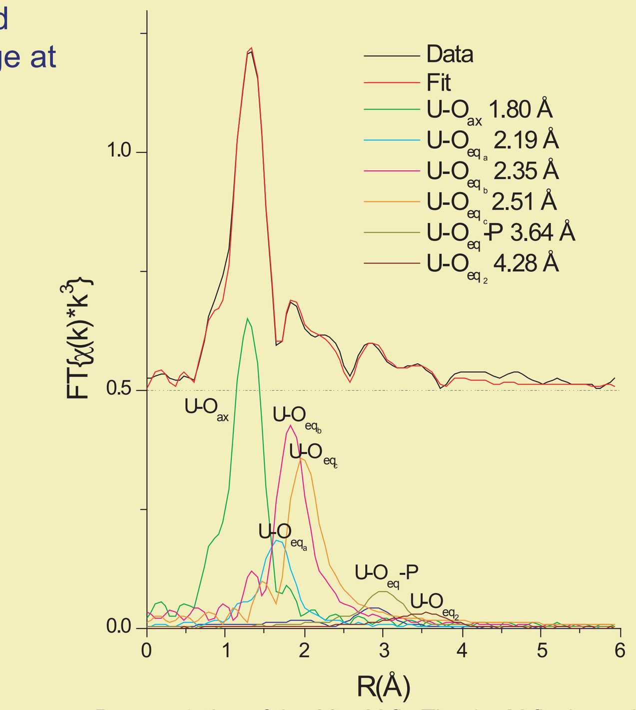


Shewanella putrefaciens. The bacteria have been shown to reduce uranium from U(VI) to U(IV).

Bacteria grown in media containing 4 mM and 22 mM uranyl acetate were killed with a 10% formaldehyde solution and refrigerated. The samples were scanned on the U L_3 edge at room temperature.



Bacteria XANES spectra. Uranium is in the Uranyl (UO_2^{2+}) form.



Deconvolution of the 22 mM fit. The 4 mM fit showed similar results.

Results

Analysis of the 22 mM and 4 mM samples revealed the uranium was bonded to a phosphate group. Because the samples were kept at room temperature for over a week before scanning, this could be the inorganic phosphate released following cell lysis. Further analysis will need to be performed.

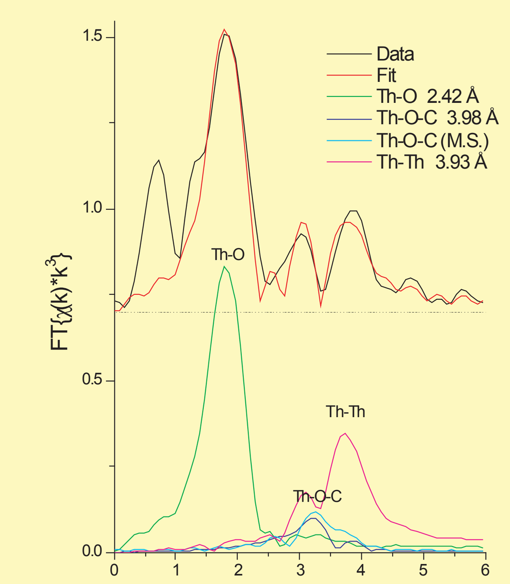
Thorium Templated Resins

Samples:

Thorium templated, nonreleased
Thorium templated, reabsorbed
Nontemplated, thorium sorbed

Results

Sample	Bond	R(Å)
Templated (nonreleased)	Th-O	2.42
	Th-O-C	3.99
	Th-Th	3.92
Templated (reabsorbed)	Th-O	2.42
	Th-O-C	3.98
	Th-Th	3.93
Nontemplated (Th absorbed)	Th-O	2.44
	Th-O-C	3.96
	Th-Th	3.90



Deconvolution of the templated thorium fit. The results for the three resins were very similar.

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